“Diffusive and convective mixing in isothermal multicomponent gaseous mixtures”.

Zhavrin U.I., Seleznev V.D., Poyarkov I.V., Fedorenko O.V.

Republic of Kazakhstan
Scientific – research Institute of theoretical and experimental physics
Tole-bi street, 96

Theory and Modeling of Thermophysical Properties.

Abstract.

Peculiarities of appearance and proceeding of anomalous free convention in isothermal multicomponent gaseous mixtures with two independent concentration gradients are studied experimentally and theoretically in present work. The reason of components anomalous separation during convective mixing consists in the dissimilar cross exchange of various kind molecules between convection counterflows occurring in the channel.

I. Introduction

Self-arbitrary penetration of one substance into another (the phenomenon known as diffusion) widespread in nature and engineering. Neither of mass transfer processes of contemporary production, for example, ammonia synthesis from natural gas, gaseous fuel combustion can be calculated without knowing the diffusion regularities. Knowing the constants of mass transfer, limited by the binary mixtures only, is already insufficient for elaboration and design of industry apparatus of chemical engineering, rocket technology in present time. However, questions of the complicated mass transfer are elucidated very incompletely in the inquiry literature. The systematic researches of multicomponent diffusion peculiarities are absent, the experimental results generalization is not conducted, but from the exiting calculation methods of the diffusion characteristics are applied in the main more simple one having received for a number of particular cases of diffusion and that's why they don't represent always the process realities. The study of multicomponent diffusion, its peculiarities, the various description methods are those problems, which stand before researchers now.

The system of Stefan-Maxwell's equations is mostly used to multicomponent mass transfer description, but as they are very complicated in practical application then either numerical integration or some approximate method, allowing to obtain enough precise results during calculations, should be used.

According to the above, the study of diffusion process in multicomponent gaseous mixtures have the scientific and practical interest, when the components concentration are commensurable and its distribution is arbitrary.

Experimental setup on the diffusion coefficient measurement in milticomponent gaseous mixtures is enough difficult problem and it demands definite qualification from the researcher and creation of original diffusion apparatuses. Unknown peculiarities of multicomponent mass transition (diffusion instability [1, 2] and the solvent gas circulation in the diffusion channel [3].) have been revealed thanks to the experiment. The study of diffusion instability (anomalous gravitation concentration convection) is interested both the mass transfer theory and the practical application.

The systems with two and more independent gradients (thermodynamic forces) are characterized by the complicated behaviour when the convective flows occur. Corresponding systems are named as the systems with “double diffusion”. The fluid systems with the concentration and temperature gradients are studied typically on this [1]. So-called stability paradox is peculiar to the systems with “double diffusion”. Instability in such systems in gravity field can occur in spite of stable stratification of the mass density (the density above is less than below).

Peculiarities of appearance and proceeding of anomalous free convention in isothermal multicomponent gaseous mixtures with two independent concentration gradients are studied experimentally and theoretically in present work.

II. Experimental research methods.

Anomalous convection occurring in ternary gaseous mixtures was found in 1966 during a study of diffusion in the three component mixtures in a Loschmidt tube [2]. Anomalous convection in quasi-steady conditions in the system of two flaks joined by a vertical capillary was first observed by one of this paper author (Zhavrin U.I.) at the beginning of the eighties. The methods widely applying for the study of diffusion in binary mixtures (the method of two flasks apparatus and the stationary flowing method) have been used for the experimental determination of the diffusion coefficients in multicomponent gaseous mixtures.

Gaseous mixtures analysis have been carried out in the chromatographs. The experimental apparatuses allow to measure the components concentration in flasks as a function of time, to record the components total concentration fluctuations by means of low-intertia sensors, as well as to visualize the flow hydrodynamics by means of a Tepler shade device.

The method of two flasks apparatus is one of the classical nonstationary methods [4], which is used during a measurement of the interdiffusion, self-diffusion, thermodiffusion coefficients and studying the diffusion baroeffect over a wide parameters range (pressure, temperature, concentration).

Quasi-steady process of the gas diffusion in the contrary directions along the capillary of cross-section area S and length L from the vessel of volume V_1 to another one of volume V_2 is considered in this method. The interdiffusion coefficient can be calculated from:

$$D_{12} = \frac{L}{St} \frac{1}{\left(\frac{1}{V_1} + \frac{1}{V_2} \right)} \ln \frac{\Delta C_0}{\Delta C_t}, \tag{1}$$

Where t - is the time of mixing process, ΔC_0 and ΔC_t is the component concentration differences in the beginning and in the end of mixing process.

Experimental technique on the apparatus of two-flask method is following. The apparatus flasks were separated between themselves and the pumping-out, for instance, of the upper flask was conducted by the backing pump. Afterwards, the corresponding gas from the bulb flushed the upper flask and then the one was filled with it to the pressure exceeding some the experiment pressure. Analogous procedure conducted with the lower flask but it was filled to the pressure less than the experiment one. When the apparatus had come to the assuming temperature rate T = (298,0 ± 0,1) K, in the flasks equalized pressure through the special tank. Absolute pressure value was determined as the sumuation of atmospheric pressure (MBP manometer – barometer was used) and the pressure measured by the manometer (excessive pressure).

The diffusion channel was opened after pressure equalization and simultaneously the stopwatch was turned on. The apparatus flasks were separated and the time of mixing was fixed after the experiment end. Gases analysis after diffusion was realized in the chromatograph both from the upper flask and the lower one of the apparatus. Having determined the component concentration after diffusion and knowing its initial concentration, the diffusion coefficient can be calculated from equation (1).

The steady flowing method has a number of advantages unlike the quasi-steady method examined above. One of main, as we consider, is opportunity to control the independent parameter (pressure difference in the ends of diffusion channel). Adjustable variation of pressure difference over the end faces of the diffusion cell let us to influence essentially on the areas and nature of diffusive and convective mixing in isothermal multicomponent gaseous mixtures. The study of mixing effects and measurement of partial flows have been carried out on the apparatus of the steady flowing method.

The main block of the apparatus is the diffusion cell which is two slotted pipelines joined by a plane slot-shaped channel of slot length 0,159 m and cross-section area (5,5

* 1,05)* 10^{-4} m^2 in which the observation window of dimension (2,0 * 5,0)* 10^{-4} m^2 with the glued-in flat-parallel glasses was embedded.

There are many methods for supplying with smooth control and measurement of the pressure difference on the diffusion channel ends, the original device (hydrostatical pressure compensator) have been described in Ref. [5]. According to Poiseuille's law, the pressure difference, created on the capillary ends, depends on viscosity and flow rate of gas or fluid, but in accordance with Pascal's law the pressure depends on gas or fluid column height.

In dependence of the research purpose any pressure differences over the end faces of the diffusion cell can be created by means of a compensation system. The compensation system consists of analyzers (the chromatograph have been used in our experiments), soap-filmy flowmeters defining the volume-flow at the exit from the diffusion cell and the compact shade device permitting to follow the mixing process nature [6]. For fixation on the videophoto equipment the eyepiece have been put away and the corresponding equipment have been situated in its place.

Thus, qualitative information about the dimensional distribution of non-uniformities and its behaviour pattern can be obtained by means of the shadow method. Note that the quantitative estimation of the results is very complicated and it requires the additional informations about the variation pattern of mixture refraction index along the line of pencil of light propagation. Figure 1 shows the shadow photographs of the typical results of mixing process received on the described apparatus.

When mixing take place in presence of convection, as shown in Fig. 1 (b), then we can observe different structural formations moving in the opposite directions in dependence on density. The studies permit us to divide conditionally all diversity of the observed convective flows in three groups: 1. chaotic flow with the set of countercurrents; 2. the "drop" regime of convection with clearly registered convective formations; 3. "stationary strata" defining the transition boarder from unstable state to the area of molecular diffusion.

The katharometal method is one of the registration methods of different convective types [7]. In particular, this method have allowed to register in dynamic all unstable mixing process from the irregular oscillations of total concentration to ordered regime and on the final stage to molecular transfer (see Fig.2). After opening the overlapping device, the oscillations are absent during some time. This testifies that formed convective structures (cells) have not run up to the kathaeometer filament yet. Then the irregular oscillations, turning with time into the attenuated periodical one, set in. From Fig. 2 we can trace the changing of oscillation regimes, moreover, in some situations the oscillating pattern of the component concentration variation attenuates and then it appears again. After chaotical regime existence of structural flows we can reveal the main oscillation frequency in spite of some higher harmonics. The main frequency and the characteristic one differ approximately 10 times, moreover, this difference remain during a great time interval. Analysis shows that two characteristic frequencies (2,0 and 1,0 Hz) exist.

Thus, analysis of time mixing evolution during anomalous instability shows the existence of the characteristic time (from the experiment it is equal to some seconds), which is necessary for convection set in as well as the existence of chaotical (turbulent), periodical and steady regimes of convective mixing.

III. Results.

Occurrence of powerful convective flows under isothermal diffusion in ternary gaseous mixtures create the components concentration redistribution, although systems were initially hydrostatically stable (the light mixtures was situated in upper flask of the apparatus, but the heavy one was in the lower flask). Thus, to carry out unstable mixing process in the simple isothermal ternary gaseous mixtures, we have to demand for diffusing mixtures [8].

Variant 1. A binary gaseous mixture (1+2) is situated in above, but pure gas (3) is in below. $\rho_2 > \rho_3 > \rho_1$; $\rho_{(1+2)} < \rho_3$; $D_{13} > D_{23}$.

Variant 2. Binary gaseous mixture (1+2) is situated in below, but pure gas (3) is in above. $\rho_2 > \rho_3 > \rho_1$; $\rho_{(1+2)} > \rho_3$; $D_{13} > D_{23}$.

Variant 3. A binary gaseous mixture (1+2) is situated in above, but a binary mixture (3+2) is in below. $\rho 2 > \rho 3 > \rho 1$; $\rho(3 + 2) > \rho(1 + 2)$; $D12 > D32$.

Variant 4. Binary gaseous mixture (1+2) and pure gas (3) can be either above or below. $\rho_2 > \rho_3 > \rho_1$; $\rho_{(1+2)} = \rho_3$; $D_{13} > D_{23}$.

In this variant unstable process can be possible under either orientation of mixtures, but only for various parameters, in particular, pressure.

In particular, gases transfer from the upper part of the diffusion apparatus in the lower one is accompanied by prevalence of the heavy component flow, that is multicomponent gaseous mixture separation occur [9].

Measured values of the effective diffusion coefficients differ many times from calculated one. Therefore, to use Fick's laws for the quantitative definitionof the mass transfer under unstable process is impossible. The mixing regime change from diffusive to convective one depends on the thermodynamic and geometric parameters of the diffusion channel.

The main factor of the experimental study of the diffusion instability regime is the registration method of the system transition boarder from one condition to another. Obviously, it can be made according to the comparison of the experimental data (for instance, concentrations of the diffused components, partial flows and etc.) with the calculated one in assumption of the stable diffusion transfer, as well as through the process visualization. As model assuming diffusive mixing, we have used the Stefan-Maxwell's equations and the solution of one, based on the linear approximation, allow to predict with confidence diffusion process. Strict definition of the stable diffusion boarder can be obtained if we observe for the partial flow ratio of components $\alpha_i = \frac{Q_{\text{эксп}\ i}}{Q_{\text{теор}\ i}}$. In Fig. 3 is shown the functional dependence α on pressure for the 0,7796 He + 0,2204R12 – Ar mixture at T = 298,0 K [10].

It is clear from Fig. 3. that this ratio begin to increase rapidly with pressure growth, that testify about occurrence of convection.

IV. Theoretical.

In accordance with the theoretical description of the observed effects, it was necessary to understand the transition reasons of stable molecular diffusion to laminar convection. As for the problems connected with the study of heat convection [1], the study of the total system of the hydrodynamic equations was taken as an approach principle.

Taking into consideration the independent diffusion condition ($\sum_{i=1}^{3}\vec{j}_i = 0$; $\sum_{i=1}^{3} C_i = 1$) we obtain the following system of equations [11]:

$$\rho\left[\frac{\partial\vec{u}}{\partial t} + (\vec{u}\nabla)\vec{u}\right] = -\nabla p + \eta\nabla^2\vec{u} + \left(\frac{\eta}{3} + \xi\right)\nabla div\vec{u} + \rho\vec{g},$$
$$\frac{\partial\rho}{\partial t} = -div(\rho\vec{\upsilon}),\ \rho\left(\frac{\partial C_i}{\partial t} + \vec{u}\nabla C_i\right) = -div\vec{j}_i, \qquad (2)$$
$$\vec{j}_1 = -\rho\left(D_{11}^*\nabla C_1 + D_{12}^*\nabla C_2\right),\ \vec{j}_2 = -\rho\left(D_{21}^*\nabla C_1 + D_{22}^*\nabla C_2\right).$$

Where D_{ij}^* - is the “practical” diffusion coefficient for ternary mixture being determined through the binary interdiffusion coefficient D_{ij} as

$$D_{11}^* = \frac{D_{13}\left[C_1D_{23} + (C_2 + C_3)D_{12}\right]}{C_1D_{23} + C_2D_{13} + C_3D_{12}},\ D_{12}^* = -\frac{C_1D_{23}(D_{12} - D_{13})}{C_1D_{23} + C_2D_{13} + C_3D_{12}},$$
$$D_{22}^* = \frac{D_{23}\left[C_2D_{13} + (C_1 + C_3)D_{12}\right]}{C_1D_{23} + C_2D_{13} + C_3D_{12}},\ D_{21}^* = -\frac{C_2D_{13}(D_{12} - D_{23})}{C_1D_{23} + C_2D_{13} + C_3D_{12}}. \qquad (3)$$

Being completed Eqs (2) and (3) by the equation of mixture state

$$\rho = \rho(C_1, C_2, p)\ ,\ T=const, \qquad (4)$$

we obtain the closed system of equations describing concentrational isothermal convection, which occur in gravity field with dimensional density non- uniformity caused by the molecular diffusion in multicomponent gaseous mixtures. Indicated phenomena resemble with the effects observed in heat convection, where its description is carried out according to the Oberbek – Businesk’s approach [12], that permit us to make use of indicated approaches.

For the study of the system of equations (2) we will apply the small disturbances method according to which the initial equations are reduced to the equations for perturbations. Further step foresees the introducing of dimensionless variables. The boundary conditions are given in dependence on the examined problem. Solution of formulated problem leads to the following equations, permitting to define the boundary values for the monotonous and oscillatory disturbances under isothermal diffusion [13]:

$$\tau_{11}\left(1 - \frac{A_2}{A_1}\tau_{12}\right)R_1 + \left(\tau_{11} - \frac{A_1}{A_2}\tau_{21}\right)R_2 = \left[(n+1)\frac{\pi}{2}\right]^4\left[\tau_{11} - \tau_{12}\tau_{21}\right] \qquad (5)$$

$$\tau_{11}\left(-\frac{A_2}{A_1}\tau_{12} - P_{22} - \tau_{11}\right)R_1 + \left(-\frac{A_1}{A_2}\tau_{21} - P_{22} - 1\right)R_2 =$$
$$= \left[(n+1)\frac{\pi}{2}\right]^4\left\{\frac{1}{P_{22}}\left(P_{22}\left[1 + \tau_{11}\right] + \tau_{11} - \tau_{12}\tau_{21}\right)\left[-P_{22} - 1 - \tau_{11}\right] - \tau_{21}\tau_{12} - \tau_{11}\right\}. \qquad (6)$$

The neutral oscillations frequency is defined as

$$\omega^2 = \frac{\left[(n+1)\frac{\pi}{2}\right]^4 \left[\tau_{12}\tau_{21} - \tau_{11}\right] + \left(1 - \frac{A_2}{A_1}\tau_{12}\right) R_1 \tau_{11} + \left(\tau_{11} - \frac{A_1}{A_2}\tau_{21}\right) R_2}{P_{22}\left(-P_{22} - 1 - \tau_{11}\right)}. \quad (7)$$

The line satisfying Eq. (6) is the neutral line for the oscillatory disturbances calculated by means of (8).

Mutual location of boundary lines (5) and (7) on the coordinate grid (*R_1, R_2*) permits us to classify the transfer regimes (see Figs.4-6).

Quadrant *$R_1 > 0$, $R_2 > 0$* corresponds to the positive density gradient. The monotonous disturbances in this area increase with the exception of the one near by the origin of coordinates where the diffusion takes place (see Figs.4).

Quadrant *$R_1 < 0$, $R_2 < 0$* corresponds to the steady state of the mixture mechanical balance; various types of oscillations, appearing in it, have the attenuated nature.

Quadrant *$R_1 > 0$, $R_2 < 0$* identifies a few regimes. The steady state of the mechanical balance is defined by the area being below the line MM. Obviously, that disturbances characterizing the area above the line MM define the monotonous instability. The area being between the lines MM and KK characterizes the system condition with oscillatory disturbances. (see Fig. 5).

Quadrant *$R_1 < 0$, $R_2 > 0$* corresponds to the regimes of the stable diffusion and monotonous instability, including the anomalous instability $(\nabla\rho < 0)$, (Fig. 6).

The points in Figs. 4 – 6 are the experimental data calculated by the formulas:

$$R_1 = \frac{gnr^4 \Delta m_1}{\rho \nu D_{11}^*} \frac{\Delta C_{10}}{L}, \quad R_2 = \frac{gnr^4 \Delta m_2}{\rho \nu D_{22}^*} \frac{\Delta C_{20}}{L}. \quad (8)$$

The shaded points correspond to convective mixing process and the unshaded one correspond to diffusion process.

Mutual location of the monotonous instability line and the zero density gradient line in Figs. 4 – 6 show that the areas, where the line MM is situated below the line corresponding to the zero density gradient, exist under certain Rayleigh numbers. In this area the mixture state is unstable with negative value of the density gradient. Physical meaning of the instability paradox for isothermal mixture was explained in Ref. 11. The medium element displacing up gets to the mixture with lesser density corresponding to the different compound. Difference in the interdiffusion coefficients of component produce the balancing of the lighter component concentration in virtue of cross diffusion and its insufficiency compensates quickly. The displacing element becomes lighter than environment and continues to float producing instability.

V. Conclusions.

The experimental study of mixing process in ternary gaseous mixtures has revealed a number of peculiarities.

1. Convective flows in a number of mixtures exceed ten or hundred times stable diffusion flows.
2. Changing condition of mixing regimes depends on parameters determining the dimensionless Rayleigh number of binary mixture, as well as the diffusion coefficient ratio.
3. Convection setting in is characterized by the delay time after beginning of mixing.

4. The monotonous and oscillatory regimes are observed clearly and defined by the increase of thermodynamical forces.

5. Convection rate has maximum under some pressure and decrease to zero both under pressure drop and one increase.

The reason of components anomalous separation during convective mixing consists in the dissimilar cross exchange of various kind molecules between convection counterflows occurring in the channel.

Such exchange can cause, in particular, the lighter component depletion of the flow directing to below, that will intensify convection because of the density difference increase of counterflows. On the one hand, this explain the high values possibility of partial flows observed in the experiments and, on the other hand, this agree to convection slowing down fact under pressure increase when the rate of the cross molecules exchange reduces in virtue of the diffusion coefficients dropping.

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Figures

Figure. 1. Shadow photographs of mixing process. First photograph (a) is the stable diffusion. Second one (b) is convective mixing.

Figure 2. Oscillating regimes in the 0,51 He + 0,49 N_2 – CH_4 system at T = 298,0K and P = 3,5 MPa.

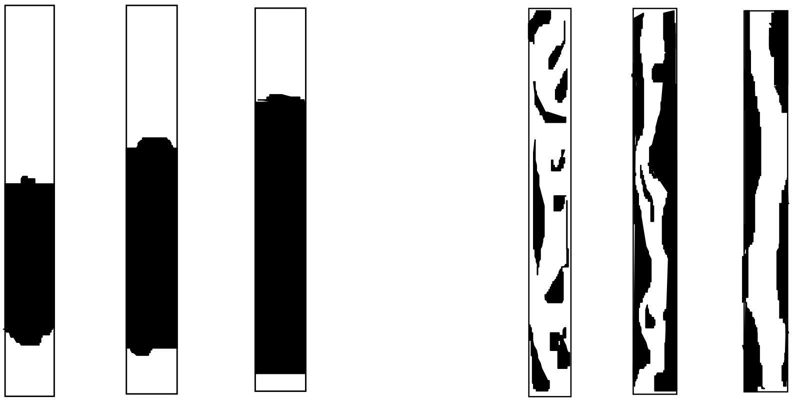
Figure 3. Dependence of parameter α on pressure in the (0,7796 He + 0,2204R12) – Ar mixture at T = 298,0 K, τ = 2 hours. The points are the experimental data. The full line is the calculation in assumption of stable diffusion. The dashed line is the experimental data approximation

Figure 4. Areas of stable and unstable diffusion in the 0.5143 He + 0.4857 Ar – 0.5148 CH_4+ 0.4852 Ar mixture at T=298.0 K and pressure range from 0.58 MPa to 3.05 MPa.

Figure 5. Areas of stable and unstable diffusion in the 0,475 He + 0,525 Ar – N_2 system, lines of monotonous and oscillatory disturbances and zero density gradient. The points are the experimental data.

Figure 6. Areas of diffusion and convective mixing in the N_2 – 0,333He + 0,667 Ar system at T = 298,0 K. Points' numbering corresponds to various pressures from 0,584 MPa to 4,51 MPa.

Figure. 1



a.

b.

Figure 2.

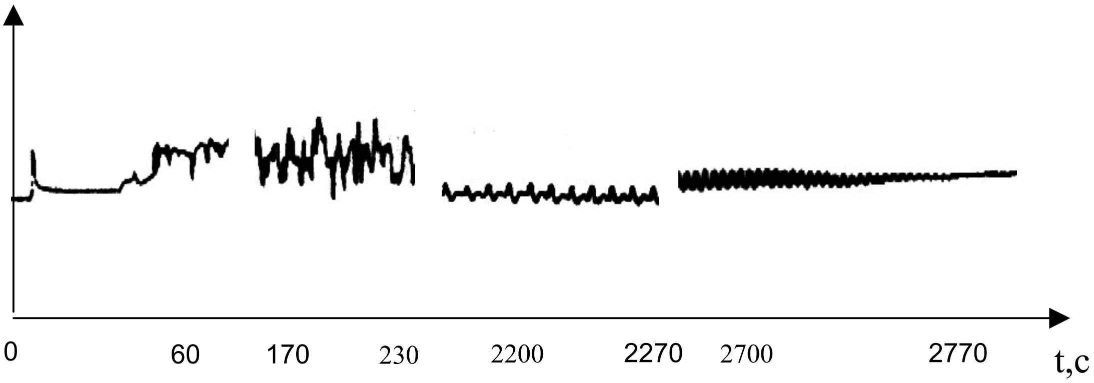


Figure 3.

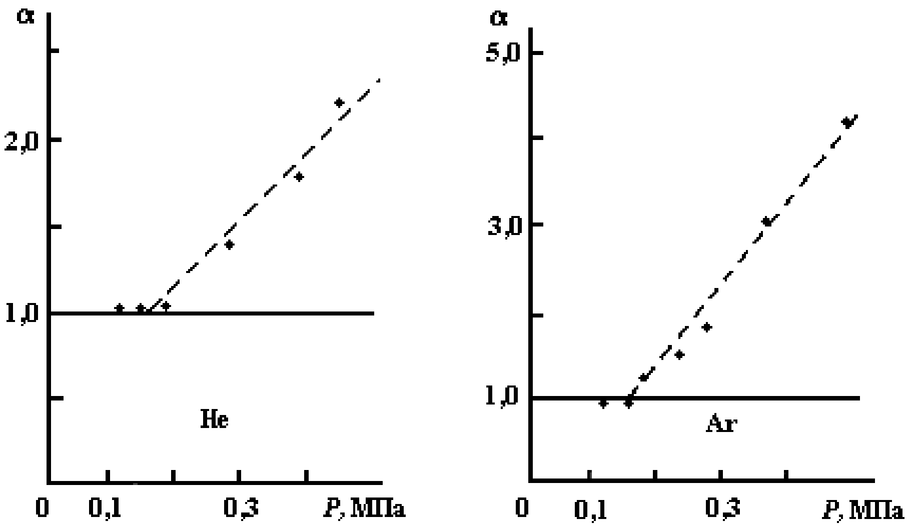


Figure 4.

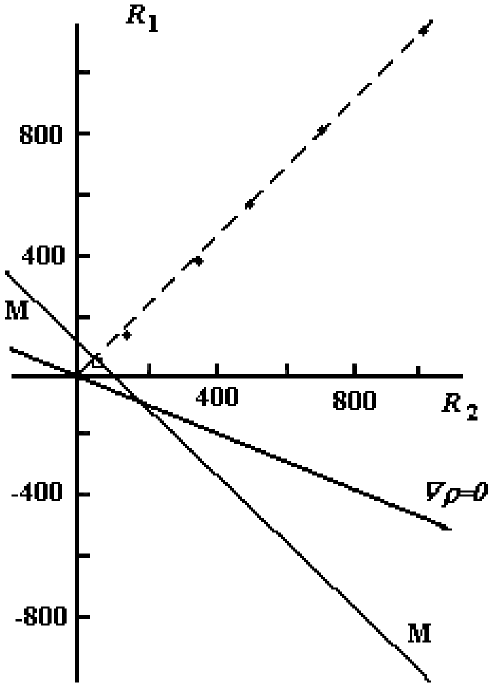
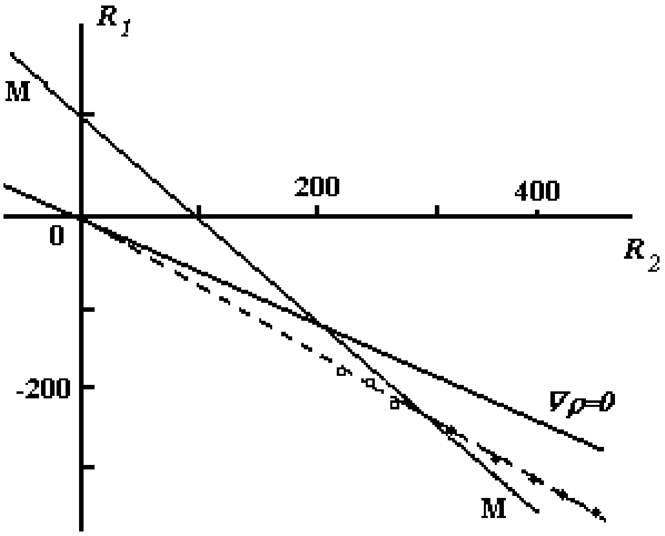
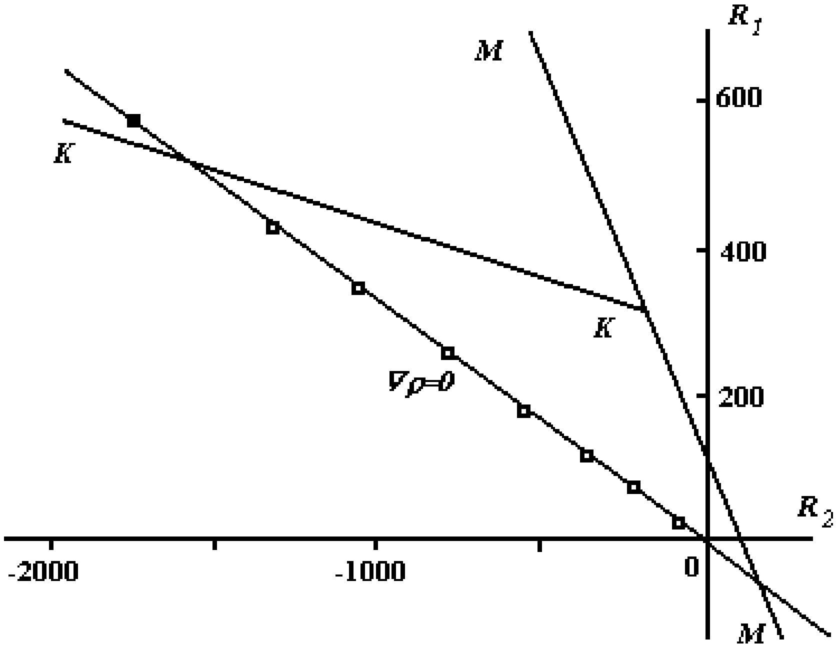


Figure 5.



Figure 6.